Modulated spin and charge densities in cuprate superconductors

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Neutron scattering experiments have played a crucial role in characterizing the spin and charge correlations in copper-oxide superconductors. While the data are often interpreted with respect to specific theories of the cuprates, an attempt is made here to distinguish those facts that can be extracted empirically, and the connections that can be made with minimal assumptions.

1. Introduction

It is well known that the parent compounds of the cuprate superconductors are antiferromagnetic insulators. When holes are doped into the ubiquitous CuO_2 planes, antiferromagnetic spin correlations survive and coexist with superconductivity. The nature of the magnetic correlations in the superconducting phases has been the subject of continuing controversy. The presence of the dynamical antiferromagnetism is believed by many to have a connection with the unusual transport properties of the cuprates.

Neutron scattering experiments have played a crucial role in characterizing the spin correlations in the cuprates. Results are often discussed in terms of specific theories, so that particular interpretations of data can become too closely associated with certain theories. This is unfortunate, as there is quite a bit of unambiguous information that one can extract directly from the neutron scattering results. When combined with complementary experimental data and rather general theoretical arguments, a striking picture of the spin and charge correlations within the CuO_2 planes emerges.

My plan of attack is as follows. The implications of the modulated charge and spin order observed in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ will be discussed first. Next, comparisions with $La_{2-x}Sr_xCuO_4$, and then $YBa_2Cu_3O_{6+x}$ will be made. A consideration of the effects of Zn-doping follows. I conclude with a brief apology to theorists.

2. $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$

The variation of the superconducting transition temperature, T_c, vs. x in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ is similar to that in $La_{2-x}Sr_xCuO_4$, except that there is a strong depression of T_c for $x \approx \frac{1}{8}$ [1]. Neutron diffraction measurements [2,3] on single crystals with $x = 0.12$ have demonstrated the existence of two kinds of incommensurate superlattice peaks, as illustrated in Fig. 1(a). Magnetic peaks are displaced from the antiferromagnetic wave vector $(\frac{1}{2}, \frac{1}{2}, 0)$ by $(\pm\epsilon, 0, 0)$ and $(0, \pm\epsilon, 0)$, with $\epsilon = 0.12$. (Wave vectors are specified in reciprocal lattice units, based on a real-space unit cell with axes **a** and **b** parallel to the Cu-O bonds.) Superlattice peaks split by an amount 2ϵ about fundamental Bragg points provide evidence for charge ordering. (The charge order is detected indirectly through nuclear displacements, but the same is generally true in x-ray diffraction studies of charge order, as well.) The charge-order peaks appear at a higher temperature than the magnetic peaks, as has recently been confirmed by x-ray scattering measurements with 100 keV x-rays [4].

Let us consider just the magnetic peaks for a moment. The appearance of peaks split in 2 orthogonal directions suggests 2 possibilities [see Fig. 1(b,c)]: 1) there are 2 types of twin domains, each with a unique modulation wave vector, or 2) there is a single type of domain with a superposition of 2 orthogonal modulations. In the latter case, one would expect to see extra magnetic peaks with splittings such as $\pm(\epsilon, \epsilon, 0)$, whereas Shamoto *et al.* [5] demonstrated the ab-

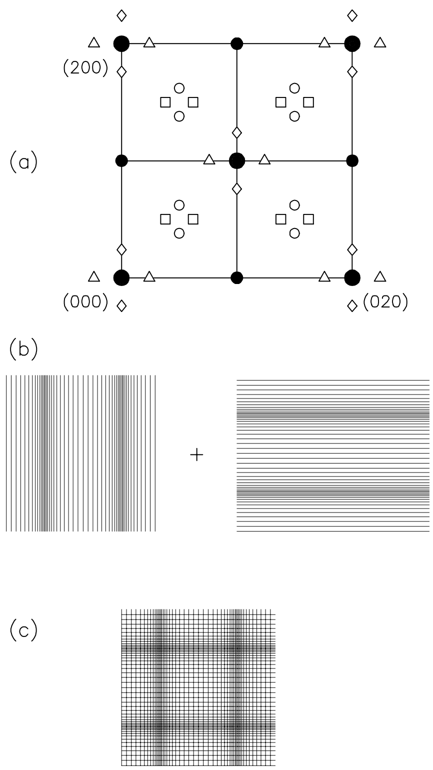

Figure 1. (a) Diagram of the $(hk0)$ zone of reciprocal space. Filled circles: Bragg points of the unmodulated lattice; open circles and squares: magnetic superlattice peaks; diamonds and triangles: charge-order superlattice peaks. (b) and (c) illustrate real-space alternatives for the modulations: (b) twin domains and (c) $2\mathbf{Q}$ structure.

sence of intensity at such positions. Besides this, there are other arguments that favor case (1). First of all, the individual CuO_2 layers in the low-temperature phase of $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ have 2-fold, but not 4-fold, symmetry, which would certainly be compatible with a uniaxial modulation. The symmetry-lowering distortion rotates by 90° from one layer to the next, thus forcing equal populations of the two types of domains. Secondly, a similar charge and spin ordering in hole-doped La_2NiO_4 has been shown to have a single modulation wave vector [6]. Finally, singly-modulated phases are quite common in nature [7], whereas doubly-modulated phases are not.

Next, there is the question of the type of spin modulation. In general, there could be a modulation of the spin direction, the spin amplitude, or a combination of the two. The existence of the charge modulation implies that there must be a modulation of the spin amplitude. Also, the modulation in the case of hole-doped La_2NiO_4 appears to involve only the spin amplitude [6]. Thus, there must be a modulation of the spin amplitude, although a component involving spin rotation is not ruled out.

Considering the spin- and charge-density modulations together, missing pieces of information are the phases of the modulations with respect to the lattice. It is not clear that the absolute phases are of crucial importance. Of greater interest is the relative phase between the two modulations. Given that the parent compound is an antiferromagnet, it seems most likely that the maxima of the charge-density modulation (corresponding to the greatest density of dopant-induced holes) should be aligned with the nodes of the magnetic modulation. In fact, it is difficult to think of a scenario in which this would not be the case.

To determine the significance of the modulations, it is necessary to evaluate their amplitudes. Of perhaps greatest interest is the amplitude of the charge modulation. One would like to know what fraction of the average hole density is spatially modulated: all or a tiny part? Unfortunately, neutron diffraction cannot provide any direct information on this matter. Instead, we must focus on the amplitude of the spin modulation. Here the issue is complicated by the fact that zero-point spin fluctuations can have a significant impact on the amplitude. An estimate from measurements on an $x = 0.12$ crystal, taking into account the lack of long-range order, yielded an amplitude of $0.10 \pm 0.03\,\mu_B$ per Cu ion [2]. Analysis of muon-spin-relaxation (μSR) measurements on a similar crystal gives the somewhat larger value of $\approx 0.3\ \mu_B$ [8]. This latter value and the observed transition temperature (≈ 30 K from μSR) appear to be consistent with the empirical curve obtained when the staggered magnetization

for a series of quasi-1D and 2D antiferromagnetic insulators is plotted versus T_N/J [8], where T_N is the Néel temperature and J is the superexchange energy. Similarly, the amplitude of the spin-density modulation in $La_2NiO_{4.125}$ is $> 80\%$ of that found in antiferromagnetic La_2NiO_4. The substantial spin-density amplitudes in these systems indicates a significant modulation of the hole density.

Any deviation from a sinusoidal modulation would be reflected in the appearance of finite intensity at higher-harmonic superlattice positions. For example, one would expect magnetic scattering to appear at positions separated by 3ϵ from the antiferromagnetic point. Such features have been measured in $La_2NiO_{4.133}$ [9]. In that case, although the intensity pattern of the harmonics is quantitatively consistent with a model of relatively squared-off magnetic domains, the strongest higher harmonic (the 3^{rd}) is only 1.5% of the 1^{st} [9]. In the case of the cuprates, such a weak harmonic would be quite difficult to detect above the background. Furthermore, transverse fluctuations of the spin and charge densities would likely damp out the harmonics.

Finally, we need to consider what is driving the modulated order. Experimentally, it is observed that the charge-order peaks appear at a higher temperature than the magnetic peaks [2]. The significance of this result can be evaluated in terms of a Landau model, which takes into account only the symmetries of the system [10]. Comparison with the phase diagram of the Landau model [10] indicates that it is the charge density that is driving the order. Charge-driven ordering is also observed in hole-doped La_2NiO_4 [11,12,9]. (If the driving force were associated with the spin density, then the charge and spin ordering temperatures would have to be identical, as found in the case of Cr [13].) Furthermore, the order of the transitions corresponds to the region of the phase diagram where only an amplitude-modulated spin density is allowed.

To summarize, the following picture of the charge and spin modulations emerges from an examination of the experimental data, especially when combined with simple theoretical arguments and analogies to related compounds. The free energy associated with the dopant-induced hole density drives the ordering, resulting in a substantial real-space modulation of the hole density. Once the hole density has ordered, the Cu spins in the hole-poor regions can order in a manner that is locally antiferromagnetic, but which flips its phase by π on crossing a maximum of the hole-density.

3. $\mathbf{La_{2-x}Sr_xCuO_4}$

The cuprate system in which incommensurate scattering was first observed is, of course, $La_{2-x}Sr_xCuO_4$ [14]. Although in this case the reported scattering is essentially all inelastic, for a given Sr content x the peak splitting ϵ [15] is essentially identical to that found in the Nd-doped case [3] (see Fig. 2). Superconductivity coexists with the incommensurate spin correlations in both systems [3,16], but T_c is strongly depressed when the correlations have a static component. Given the similar $\mathbf{Q}$ dependence of the magnetic scattering and the associated superconductivity in the two systems, it seems clear that the spin correlations must have the same fundamental nature. It follows that, since the modulated antiferromagnetism in the Nd-doped system is driven by the spatially oscillating hole density, a dynamic charge modulation is implied in the case of $La_{2-x}Sr_xCuO_4$.

A wider range of Sr concentrations has been studied in the system without Nd, and the variation of ϵ with x shows an interesting trend. For $x > 0.05$, ϵ initially increases linearly with x before saturating for $x > 1/8$ [15,17]. Since ϵ is proportional to the inverse of the charge modulation period, the $\epsilon \sim x$ behavior suggests that the amplitude of the charge modulation remains constant while the period decreases with increasing x. (A very similar trend is observed in hole-doped La_2NiO_4 [12].) This is consistent with an effective segregation of the doped holes, such that an initially antiferromagnetic CuO_2 plane is broken up into antiferromagnetic strips, with the strips becoming narrower as the hole density increases. (At small x, the pinning of holes by the randomly distributed dopants dominates [18] and inhibits any well-defined periodic charge modula-

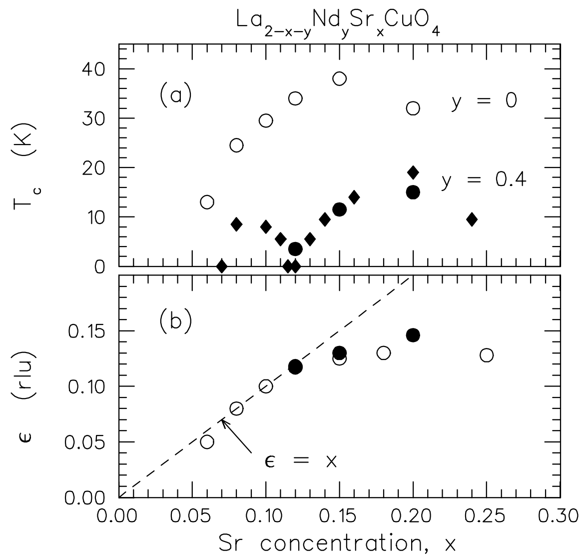

Figure 2. Results for T_c and ϵ as a function of x in $La_{2-x-y}Nd_ySr_xCuO_4$. Open circles: $y = 0$ [15]; filled circles (diamonds): single-crystal (ceramic) samples with $y = 0.4$ [3].

tion. The effect of pinning by Sr ions is even greater in $La_{2-x}Sr_xNiO_4$ [12].) The saturation of ϵ for $x > 1/8$ clearly indicates that the period of the modulation remains constant in that region, even though the charge density continues to increase.

Are there big differences between samples with and without Nd doping? Not really. The main effect of the Nd, which has the same valence as La, is associated with its small ionic radius relative to Sr. Its presence induces a change from the usual low-temperature-orthorhombic (LTO) phase to the low-temperature-tetragonal (LTT) phase below about 70 K [1], similar to the transition first observed in $La_{1.88}Ba_{0.12}CuO_4$ [19]. The difference between the two structures involves a subtle variation in the tilt pattern of CuO_6 octahedra. The atomic displacement pattern in the LTT phase is compatible with a coupling to the charge modulation, and hence with static charge order. In $La_{2-x}Sr_xCuO_4$, the phonon associated with the same displacement pattern is quite soft ($\hbar\omega \approx 1.5$ meV [20]), so that it is possible that a charge modulation, though not static, could be slowly fluctuating with the lattice vibrations.

The picture of antiferromagnetic strips interacting weakly across hole-rich domain walls suggests that the spin excitations would be modified in a modest way relative to those in the parent compound. Indeed, inelastic neutron scattering measurements on stripe-ordered $La_2NiO_{4.133}$ indicate the low-energy spin excitations disperse away from the incommensurate peak positions with an effective spin-wave velocity that is 60% of that in undoped La_2NiO_4 [21]. Such a renormalization can be understood in large part as occuring due to the reduction in the average number of nearest-neighbor spins to which there is a strong coupling J, with no significant change in J. Inelastic measurements on $La_{2-x}Sr_xCuO_4$ [14,22,23] appear to be compatible with such a picture [24]. A reduced dispersion, limited by a finite correlation length, is observed at low energies [14,22], while high-energy measurements indicate that the maximum excitation frequency is reduced by about 20% relative to La_2CuO_4 [23].

4. $YBa_2Cu_3O_{6+x}$

In $YBa_2Cu_3O_{6+x}$, the antiferromagnetic spin correlations become completely dynamic for $x \geq 0.5$ [25,26]. Although most neutron scattering studies have detected a dynamical spin susceptibility that is peaked commensurately at the antiferromagnetic wave vector, the **Q** width of the scattering measured for $\hbar\omega < 30$ meV increases roughly linearly with x [26], in a manner similar to the variation of ϵ with x in $La_{2-x}Sr_xCuO_4$. The **Q** dependence of the line shape for the low-energy range and $x \sim 0.5$–0.6 has been shown to be more complex than a simple commensurately-centered gaussian [27]. Recently it was pointed out that the latter results can be modelled in a fashion similar to the incommensurate excitations in $La_{2-x}Sr_xCuO_4$ if one allows for a shorter spin-spin correlation length [24].

In a new study of a crystal of $YBa_2Cu_3O_{6.5}$ with $T_c = 52$ K, Bourges *et al.* [28] have extended inelastic scattering measurements up to excitation energies of 120 meV. In this good su-

perconductor they have detected distinct spin excitations that are very similar to the acoustic and optic spin-wave modes observed previously in antiferromagnetic $YBa_2Cu_3O_{6.2}$ [29]. Furthermore, at energies > 30 meV the excitations show an apparent dispersion with a velocity $\sim 65\%$ of that found in the antiferromagnetic. This renormalization is quite similar to that found in the doped-nickelate case [21]. The close connection between the spin excitations in the superconducting and antiferromagnetic $YBa_2Cu_3O_{6+x}$ suggests that they are caused by similar clusters of antiferromagnetically correlated Cu spins, and the existence of such clusters in the superconducting sample requires a spatial segregation of the doped holes.

Dai, Mook, and Doğan [30] have just reported evidence for incommensurate magnetic fluctuations in $YBa_2Cu_3O_{6.6}$ with $T_c = 62.7$ K. The incommensurability is observed in both energy-integrated scans and constant-E scans at $\hbar\omega = 24$ and 27 meV. It is suggested that the modulation direction is parallel to the antiferromagnetic wave vector (i.e., rotated by 45° relative to the $La_{2-x}Sr_xCuO_4$ case). These results appear to provide a very direct connection between the spin correlations in superconducting $YBa_2Cu_3O_{6+x}$ and $La_{2-x}Sr_xCuO_4$.

5. Zn Doping

So far, I have presented arguments that neutron scattering studies indicate an intrinsic segregation of doped holes in the form of a periodic density modulation within the CuO_2 planes. If this interpretation is correct, then one might expect that, besides special modifications of the crystal structure, there would be other ways to pin the charge and spin modulations. Indeed, light doping with Zn appears to be another such way.

Koike *et al.* [31] have shown that sustitution of 1% Zn for Cu in $La_{2-x}Sr_xCuO_4$ is sufficient to cause a drastic dip in T_c as a function of x, with the minimum occurring at $x = 0.115$. The resulting phase diagram looks reminiscent of that for Nd-doped samples [1], except for the lack of evidence for a change in lattice distortion. New neutron scattering results on a crystal of $La_{1.86}Sr_{0.14}Cu_{0.988}Zn_{0.012}O_{4-\delta}$ with $T_c = 19$ K by Hirota *et al.* [32] show that the Zn does not modify the incommensurability of the magnetic scattering, but does shift spectral weight to lower energies and induces a sharp (in **Q**) elastic component that grows below ~ 30 K. The coexistence of superconductivity and static modulated spin order is consistent with observations in Nd-doped samples [3].

Zn-doped $YBa_2Cu_3O_{6+x}$ samples with a range of oxygen concentrations have also been studied by neutron scattering [33]. The results are qualitatively similar to the 214 case: Zn-doping does not modify the **Q** dependence of the scattering, but it shifts spectral weight from higher energies to the low-energy region.

It is rather interesting to note that the effect of Zn on the superconducting cuprates is empirically quite similar to the effect of Zn-doping on spin-ladder and spin-Peierls compounds [34,35]. Both of the latter systems, without Zn, have energy gaps in their spin excitations. Very small amounts of Zn cause the coexistence of excitations within the gap and even local antiferromagnetic order.

6. Conclusion

In this paper I have attempted to present a consistent interpretation of neutron scattering measurements on a range of systems, one that I believe is suggested directly by the data. I hope that I have persuaded the reader that $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$, rather than being a pebble in the collective shoe on the long march toward an understanding of the cuprates, is actually a Rosetta stone for deciphering the experiments. Specific microscopic theories for the cuprates have been deliberately ignored here; hopefully, any theorists who read this paper will feel equitably treated. Of course, finding the connection between the strong electronic correlations indicated by experiments, on the one hand, and superconductivity, on the other, is entirely the province of theorists, from whom, undoubtedly, a great deal of "discussion" will continue to be heard.

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